Abstract

Thermoelectric (TE) materials directly convert heat energy into electrical energy. The conversion efficiency of the TE devices depends on the performance of the materials. The conversion efficiency of available thermoelectric materials and devices is low. Therefore, the development of new materials for improving thermoelectric device performance is a highly essential. As the performance of the TE materials depends on TE figure of merit [zT=$\frac{S^2}{\rho\lambda}T$] which consist of three material properties such as Seebeck coefficient (S), electrical resistivity (ρ) and thermal conductivity (λ). Thermoelectric figure of merit can be improved by either increase of power factor or decreasing of thermal conductivity or by both. In the present thesis, Cu based chalcogenide compounds are chosen for the study of thermoelectric properties because of their complex crystal structure, which leads to lower values of thermal conductivity. Also, the power factor of these materials can be tuned by the partial substitution /doping. In the present thesis, Cu based chalcogenide compounds: quaternary chalcogenide compound ($Cu_2ZnSnSe_4$), ternary compounds (Cu_2SnSe_3 and Cu_2GeSe_3) and tetrahedrite materials ($Cu_{12}Sb_4S_{13}$) have been prepared by solid state synthesis. The prepared compounds are characterized by XRD for the phase identification, Raman Spectroscopy used as complementary technique for XRD, SEM for surface morphology and EPMA for the phase purity and elemental composition analysis respectively. For the evaluation of zT, thermoelectric properties of all the samples have been studied by measuring Seebeck coefficient, resistivity and thermal diffusivity. In the chapter 1, a brief introduction about thermoelectricity and its effects is discussed. Thermoelectric materials parameters such as electrical resistivity, Seebeck coefficient and thermal conductivity for different class of materials are mentioned. The selection of thermoelectric materials and the motivation for choosing the Cu based chalcogenide compounds for thermoelectric applications are discussed.

In chapter 2, the details of the experiments carried out for Cu based chalcogenide compounds are presented.

In chapter 3, the effect on thermoelectric properties by the cation substitution on quaternary chalcogenide compound $Cu_{2+x}ZnSn_{1-x}Se_4$ (0, 0.025, 0.05, 0.075, 0.1, 0.125, and 0.15) is studied. The electrical resistivity of all the samples decreases with an increase in Cu content except for $Cu_{2.1}ZnSn_{0.9}Se_4$, most likely due to a

higher content of the ZnSe. All the samples showed positive Seebeck coefficients indicating that holes are the majority charge carriers. The thermal conductivity of doped samples was higher as compared to $Cu_2ZnSnSe_4$ and this may be due to the larger electronic contribution and the presence of the ZnSe phase in the doped samples. The maximum zT = 0.23 at 673 K is obtained for $Cu_{2.05}ZnSn_{0.95}Se_4$.

In chapter 4, the effect of multi–substitution of $Cu_{2.1}ZnSn_{1-x}In_xSe_4$ (0, 0.05, 0.075, and 0.1) on transport properties were studied. The Rietveld powder X-ray diffraction data accompanied by electron probe microanalysis (EPMA) and Raman spectra of all the samples confirmed the formation of a tetragonal kesterite structure. The electrical resistivity of all the samples exhibits metallic-like behavior. The positive values of the Seebeck coefficient and the Hall coefficient reveal that holes are the majority charge carriers. The co-doping of copper and indium leads to a significant increase of the electrical resistivity and the Seebeck coefficient as a function of temperature above 650 K. The thermal conductivity of all the samples decreases with increasing temperature. Lattice thermal conductivity is not significantly modified as the doping content may infer negligible mass fluctuation scattering for copper/zinc and indium/tin substitution. Even though, the power factors ($\frac{S^2}{\rho}$) of indium-doped samples $Cu_{2.1}ZnSn_{1-x}In_xSe_4$ (x=0.05, 0.075) are almost the same, the maximum zT=0.45 at 773 K was obtained for $Cu_{2.1}Zn_{0.9}Sn_{0.925}In_{0.075}Se_4$ due to its smaller value of thermal conductivity.

In chapter 5, thermoelectric properties of Zn doped ternary compounds $Cu_2Zn_xSn_{1-x}Se_3$ (x = 0, 0.025, 0.05, 0.075) were studied. The undoped compound showed a monoclinic crystal structure as a major phase, while the doped compounds showed a cubic crystal structure confirmed by powder XRD (X-Ray Diffraction). The electrical resistivity decreased up to the samples with Zn content x=0.05 in $Cu_2Zn_xSn_{1-x}Se_3$, and slightly increased in the sample $Cu_2Zn_{0.075}Sn_{0.925}Se_3$. This behavior is consistent with the changes in the carrier concentration confirmed by room temperature Hall coefficient data. Temperature dependent electrical resistivity of all samples showed heavily doped semiconductor behavior. All the samples exhibit positive Seebeck coefficient (S) and Hall coefficient indicating that the majority of the carriers are holes. A linear increase in Seebeck coefficient with increase in temperature indicates the degenerate semiconductor behavior. The total thermal conductivity of the doped samples increased with a higher amount of doping, due to the increase in the carrier contribution.

The total and lattice thermal conductivity of all samples decreased with increasing of temperature, which points toward the dominance of phonon scattering at high temperatures.The maximum zT = 0.34 at 723 K is obtained for the sample Cu_2SnSe_3 due to a low thermal conductivity compared to the doped samples.

In chapter 6, thermoelectric properties of $Cu_2Ge_{1-x}In_xSe_3$ (x = 0, 0.05, 0.1, 0.15) compounds is studied. The powder X-ray diffraction pattern of the undoped sample revealed an orthorhombic phase. The increase in doping content led to the appearance of additional peaks related to cubic and tetragonal phases along with the orthorhombic phase. This may be due to the substitutional disorder created by indium doping. The electrical resistivity (ρ) systematically decreased with an increase in doping content, but increased with the temperature indicating a heavily doped semiconductor behavior. A positive Seebeck coefficient (S) of all samples in the entire temperature range reveal holes as predominant charge carriers. Positive Hall coefficient data for the compounds $Cu_2Ge_{1-x}In_xSe_3$ (x= 0, 0.1) at room temperature (RT) confirm the sign of Seebeck coefficient. The trend of as a function of doping content for the samples $Cu_2Ge_{1-x}In_xSe_3$ with x = 0 and 0.1 agrees with the measured charge carrier density calculated from Hall data. The total thermal conductivity increased with rising doping content, attributed to an increase in carrier thermal conductivity. The thermal conductivity decreases with increasing temperature, which indicates the dominance of Umklapp phonon scattering at elevated temperatures. The maximum thermoelectric figure of merit (zT) = 0.23 at 723 K was obtained for $Cu_2In_{0.1}Ge_{0.9}Se_3$.

In chapter 7, thermoelectric properties of $Cu_{12-x}Mn_{1-x}Sb_4S_{13}$ (x = 0, 0.5, 1.0, 1.5, 2.0) samples were studied. The Rietveld powder XRD pattern and Electron Probe Micro Analysis revealed that all the Mn substituted samples showed a single tetrahedrite phase. The electrical resistivity increased with increasing Mn due to substitution of Mn^{2+} on the Cu^{1+} site. The positive Seebeck coefficient for all samples indicates that the dominant carriers are holes. Even though the thermal conductivity decreased as a function of increasing Mn, the thermoelectric figure of merit (zT) decreased, because the decrease of the power factor is stronger than the decrease of the thermal conductivity. The maximum zT = 0.76 at 623 K is obtained for $Cu_{12}Sb_4S_{13}$.

In chapter 8, the summary and conclusion of the present work is presented.